

## **Adsorption of CO<sub>2</sub> on Molecular sieves and Activated Carbon**

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### **Introduction**

Fossil fuels supply more than 98% of the world's energy needs. However, the combustion of fossil fuels is one of the major sources of the greenhouse gas CO<sub>2</sub>. It is necessary to develop technologies that will allow us to utilize the fossil fuels while reducing the emissions of greenhouse gases. Commercial CO<sub>2</sub> capture technology that exists today is very expensive and energy intensive. Improved technologies for CO<sub>2</sub> capture are necessary to achieve low energy penalties.

Pressure swing adsorption (PSA) is one of the potential techniques that could be applicable for removal of CO<sub>2</sub> from gas streams.

PSA processes are based on preferential adsorption of the desired gas (eg. CO<sub>2</sub>) on a porous adsorbent at high pressure, and recovery of the gas at low pressure. Thus, the porous sorbent can be reused for subsequent adsorption. PSA technology has gained interest due to low energy requirements and low capital investment costs<sup>1,2</sup>. Applications of PSA processes to separation/capture of carbon dioxide are also reported<sup>3,4</sup>. Low recovery rate of CO<sub>2</sub> is one of the problems reported with the PSA processes. Development of regenerable sorbents that have high selectivity, high adsorption capacity, and high desorption rate for CO<sub>2</sub> adsorption/desorption

is critical for the success of the PSA process.

In this work three sorbents namely, molecular sieve 13X, molecular sieve 4A, and activated carbon from Süd Chemie Inc., that can be utilized in the PSA process for recovery of  $\text{CO}_2$  were studied. Volumetric adsorption studies of  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2$  on the three sorbents were conducted at  $25^\circ\text{C}$  and up to a pressure of 300 psi ( $\sim 2 \times 10^6$  Pa) to determine the equilibrium adsorption capacity of these materials. The adsorption isotherms of these materials at pressures up to 300 psi are not reported in the literature. Studies on competitive adsorption of  $\text{CO}_2$  from gas mixtures were conducted utilizing an atmospheric micro reactor. Elemental characterizations of these sorbents were conducted utilizing advanced analytical techniques such as X-ray photoelectron spectroscopy and scanning electron microscopy/energy dispersive spectroscopy.

## **Experimental**

The three sorbents namely, Zeochem-Z10-02/molecular sieve 13X (8x12 mesh), Zeochem Z4-01/molecular sieve 4A (4x8 mesh) and G-32 H activated carbon (4x10 mesh) were obtained from Süd Chemie Inc.. Adsorption isotherms at  $25^\circ\text{C}$  of pure  $\text{CO}_2$  (99.5%, Jackson Welding Supply Co.),  $\text{N}_2$  (99.5%, Jackson Welding Supply Co.), and  $\text{H}_2$  (99.95%, Butler Gas Products Co.) on the three sorbents were obtained up to an equilibrium pressure of about 300 psi ( $\sim 2 \times 10^6$  Pa) utilizing a volumetric adsorption apparatus. Approximately 10 ml of the sorbent materials were placed in the sample chamber and were evacuated to  $\sim 5 \times 10^{-5}$  Torr. The amount of  $\text{CO}_2$  adsorbed was calculated utilizing the pressure measurements before and after the exposure of the sample chamber to  $\text{CO}_2$ . Base line data with  $\text{CO}_2$  were obtained utilizing 10 ml of glass beads (2mm

diameter). Nine adsorption cycles were performed with each sorbent. After each cycle the sorbent was evacuated to about  $5 \times 10^{-5}$  Torr overnight. Cycles 1,2,3,4,7 and 10 were performed with CO<sub>2</sub>, cycles 5 and 6 were performed with nitrogen and cycles 8 and 9 were performed with hydrogen.

BET nitrogen surface areas of the materials were measured utilizing Micromeritics surface area and pore volume analyzer. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Physical Electronics Model SAM 590 equipped with a model 15-255 GAR analyzer and a 15 kV X-ray source from Physical Electronics<sup>5</sup>. The system was routinely operated within a pressure range of  $1.3 \times 10^{-7}$  to  $1.3 \times 10^{-6}$  Pa ( $10^{-9}$ - $10^{-8}$  Torr). The instrument was calibrated using the photoemission lines  $E_B(\text{Cu } 2P_{3/2}) = 932.4$  eV and  $E_B(\text{Au } 4f_{7/2}) = 83.8$  eV. The binding energies were referenced to the C(1s) level at 284.6 eV for adventitious carbon. All intensities reported are experimentally determined peak areas divided by the instrumental sensitivity factors. Spectra were obtained with about five different samples and the intensity and binding energy values reported are the averages of values obtained from all sets of data. X-ray microanalysis was carried out using JOEL 840A model scanning electron microscope (SEM) . The electron microscope is equipped with a Noran Instruments energy-dispersive spectrometer<sup>6</sup>. The SEM was interfaced to a Noran Instruments Voyager-IV X-Ray analysis and image processing unit. Resolution based on the Mn K $\alpha$  energy line was 149 eV.

The competitive adsorption studies at 25 °C were conducted utilizing Micromeritics Autochem 2910 atmospheric microreactor. The composition of the two gas mixtures utilized were 14.8 % CO<sub>2</sub> and 85.2% N<sub>2</sub>, and 10% CO<sub>2</sub>, 28% H<sub>2</sub> and 62% He. The analysis of the outlet gas stream

was conducted utilizing a Pfeiffer Vacuum Thermostar mass spectrometer. The samples were pre-treated at 250 °C for one hour in the microreactor under helium prior to the exposure to the gas mixtures containing CO<sub>2</sub>.

## **Results and Discussion**

### Adsorption Isotherms

Volumetric adsorption isotherms of CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub> on molecular sieve 13X at 25 °C are shown in Figure 1. The shape of the of the isotherms appear to be similar to type 1(Langmuir). The CO<sub>2</sub> adsorption increased rapidly when the pressure was increased up to 50 psi. The increase in CO<sub>2</sub> adsorption after 50 psi appears to be gradual. The adsorption isotherms for repeated cycles were very similar. This indicated that the adsorption is fully reversible and complete regeneration can be obtained by evacuation of the material after adsorption. At all pressures, adsorption isotherms of both nitrogen and hydrogen were lower than those of CO<sub>2</sub>. Both nitrogen and hydrogen isotherms were also completely reversible. Preferential adsorption of CO<sub>2</sub> on molecular sieve 13X indicates that this material can be used for separation of CO<sub>2</sub> from some gas mixtures. The final adsorption isotherm (cycle 9 which was obtained after the completion of adsorption experiments with nitrogen and hydrogen) was conducted with CO<sub>2</sub> and it was very similar to the previous adsorption isotherms with CO<sub>2</sub>. This indicated that the sorbent was not affected by the adsorption of nitrogen and hydrogen.

The volumetric adsorption isotherms for molecular sieve 4A are shown in Figure 2. The adsorption isotherms indicate that the uptake of CO<sub>2</sub> was higher than that of the other two gases,

nitrogen and hydrogen. This preferential uptake of  $\text{CO}_2$  indicates that this sorbent may be suitable for the separation of  $\text{CO}_2$  from gaseous mixtures. The adsorption isotherm of  $\text{CO}_2$  for molecular sieve 4A during the first cycle was higher than that of the following cycles, indicating that the adsorption was not completely reversible. The adsorption at the first cycle was the highest. The average pore diameter of molecular sieve 4A is 4 Angstroms while the average pore diameter of molecular sieve 13X is about 10 Angstroms. The kinetic diameter of  $\text{CO}_2$  molecule is 3.9 Angstroms which is only slightly lower than the pore diameter of molecular sieve 4A<sup>7</sup>. So the mobility of the  $\text{CO}_2$  molecule may be restricted inside the pores of molecular sieve 4A. The incomplete desorption of  $\text{CO}_2$  after the first adsorption cycle in molecular sieve 4A may be due to the smaller pore size. However, the amount of  $\text{CO}_2$  adsorbed was constant after the second cycle. This indicates that after the second cycle, a constant amount of  $\text{CO}_2$  may be desorbed at each cycle. The uptake of  $\text{CO}_2$  for molecular sieve 4A was lower than that of molecular sieve 13X at all equilibrium pressures up to 300 psi. However, both nitrogen and hydrogen adsorption isotherms of molecular sieve 4A appear to be similar to those of molecular sieve 13X. The adsorption of nitrogen and hydrogen did not appear to adversely affect the adsorption capacity of the sorbent for  $\text{CO}_2$  adsorption.

The adsorption isotherms of  $\text{CO}_2$  on activated carbon are shown in Figure 3. It is interesting to note that all the isotherms were extremely reproducible, which indicates the excellent reversibility of adsorption. The  $\text{CO}_2$  uptake of activated carbon was lower than that for the two molecular sieves at lower pressures (< 30 psi), but at higher pressures the  $\text{CO}_2$  uptake of activated carbon was higher than that of the molecular sieves. Nitrogen and hydrogen adsorption isotherms on

activated carbon were also very reproducible. The final CO<sub>2</sub> adsorption cycle (cycle 10) was very similar to the first cycle, which indicated that the CO<sub>2</sub> adsorption capacity of the sorbent was not affected by the adsorption of other gases.

The ratio of the moles of adsorbed CO<sub>2</sub> to nitrogen is shown in Figure 4. The ratio of CO<sub>2</sub>/nitrogen decreased with increasing pressure and appeared to remain constant above 150 psi in all three sorbents. This indicates that the selectivity of the sorbents for CO<sub>2</sub> adsorption is better at lower pressures even though the total CO<sub>2</sub> adsorption was higher at higher pressures. At lower pressures, this selectivity molar ratios appear to be higher for the molecular sieves than that for the activated carbon but were similar at higher pressures. Similar observations were made with the adsorbed mole ratios of CO<sub>2</sub>/hydrogen on the three sorbents.

Adsorption isotherms of CO<sub>2</sub> (best isotherm selected from the repeated cycles) with adsorption denoted in moles/kg and moles/liter, for three adsorbents are shown in Figures 5 and 6 respectively. Both molecular sieves 13X and 4A exhibited higher uptake of moles of CO<sub>2</sub> per kg of the sorbent at pressures less than 30 psi, but at higher pressures activated carbon showed higher CO<sub>2</sub> uptake. When the CO<sub>2</sub> uptake was in moles/liter, the activated carbon showed higher CO<sub>2</sub> uptake at pressures above 100 psi.

Isosteric heats of adsorption as a function of surface coverage were calculated using adsorption isotherms at different temperatures (30, 40, 50 °C). The Clausius-Clapeyron equation was utilized in these calculations<sup>8</sup>. Isosteric heats of adsorption of molecular sieve 13X decreased

from 50 to 10 kJ mol<sup>-1</sup> with increasing coverage from 1 to 5 moles kg<sup>-1</sup>. For the activated carbon, the isosteric heats of adsorption decreased from 28 to 11 kJmol<sup>-1</sup> with increasing coverage. The wide range of activation energies observed for the molecular sieve 13X indicated that there is a wide range of sites with varying adsorption energies present in molecular sieve 13X.

### Characterization of Adsorbents

Since molecular sieve 13X and activated carbon showed reversible adsorption most of the characterization work was done with these two sorbents. The nitrogen BET surface areas of molecular sieves 13X and activated carbon were 506 and 897 m<sup>2</sup>/g respectively. The high surface area of activated carbon may have contributed to the high CO<sub>2</sub> uptake at higher pressures. The CO<sub>2</sub> uptake values per unit surface area are shown in Figure 7. It is interesting to note that the moles CO<sub>2</sub> adsorbed per unit area is higher on molecular sieve 13X than that on activated carbon. These values were similar on both materials only at about 250-300 psi . This indicates that the surface of molecular sieve 13X has a better affinity for CO<sub>2</sub> than that of activated carbon.

The cross sectional area<sup>9</sup> of the CO<sub>2</sub> molecule is 19.5 Angstrom<sup>2</sup>. If closed packing of CO<sub>2</sub> is assumed, at a monolayer coverage the surface should occupy about 8.5x10<sup>-6</sup> moles per meter<sup>2</sup>. From the adsorption isotherms it was determined that the molecular sieve 13X has about 9.9x10<sup>-6</sup> moles of CO<sub>2</sub> per m<sup>2</sup> at saturation coverage (250-300 psi) and this is very close to the value corresponding to a close packed monolayer coverage of CO<sub>2</sub>. The saturation CO<sub>2</sub> coverage of activated carbon as determined by the adsorption isotherms is about 9.5x10<sup>-6</sup> moles/m<sup>2</sup>. This indicates that a close pack monolayer of CO<sub>2</sub> is also formed at saturation with the activated

carbon. So both these materials utilize the complete surface area to form a close packed monolayer at higher pressures.

The skeletal and bulk densities of molecular sieve 13X as measured by mercury porosimetry were 1.87 and 1.06 g/cc respectively and for activated carbon these values were 1.14 and 0.94 g/cc respectively. So the density of activated carbon was lower than that of the molecular sieve 13X. The elemental analysis of the bulk and the surface of the sorbents are listed in Table I. The major elements observed at the surface of the molecular sieves were Si, Al and Na. Trace amounts of K, Ca and Fe were also observed. The ratio of the K/Si of molecular sieve 13X was considerably higher at the surface than that at the bulk. This indicates that most of the K resides on the surface of the molecular sieve 13X. Surface analysis of the activated carbon indicated that there were Al, K and trace amounts of Cl, Na, S and Si on the surface. Both Al/Si and K/Si ratios were substantially higher at the surface of activated carbon than at the bulk as shown in Table I. This indicated that the potassium resides mainly on the surface of the activated carbon, similar to the observations with molecular sieve 13X. Elemental distributions of the cross sections of the pellet of molecular sieve 13X are shown in Figure 8. It is clear that all the elements including the trace elements are well distributed in the pellet. Since the chemical compositions of molecular sieve 13X and activated carbon are completely different, it is difficult to relate the adsorption properties to the chemical composition of the surfaces.

#### Competitive Adsorption Studies from Gas Mixtures Containing CO<sub>2</sub>

Results of the competitive gas adsorption studies conducted utilizing 14.8 % CO<sub>2</sub> and 85.2% N<sub>2</sub>



on molecular sieve 13X in the atmospheric micro reactor are shown in Figure 9. The gas mixture was introduced to 1.5 g of molecular sieve 13 X at a flow rate of 15 cc/min and at 25 °C. After the introduction of the gas mix to the molecular sieve 13X, the CO<sub>2</sub> concentration decreased to almost zero while the nitrogen concentration increased to 100%, until the breakthrough. This indicates that an excellent separation of CO<sub>2</sub> from a gas mixture of N<sub>2</sub> and CO<sub>2</sub> can be obtained with molecular sieve 13X. The amount of CO<sub>2</sub> adsorbed per kg of the sorbent as a function of time, calculated from the data is shown in Figure 10. There is a linear uptake of CO<sub>2</sub> with time and the total amount of CO<sub>2</sub> adsorbed at the breakthrough or saturation was about 2.1 moles/kg of the sorbent. This value is very similar to the amount of CO<sub>2</sub> adsorbed at 1 atm from volumetric equilibrium adsorption studies, as shown in Figure 1. This indicates that the full capacity of the molecular sieve 13X was utilized for CO<sub>2</sub> adsorption during competitive gas adsorption from a CO<sub>2</sub> and N<sub>2</sub> mixture. A similar observation was made with molecular sieve 13X during competitive CO<sub>2</sub> adsorption from a gas mixture containing 10% CO<sub>2</sub>, 28% H<sub>2</sub> and 62% He as shown in Figure 11. It was also possible to obtain an excellent separation of CO<sub>2</sub> from the gas mixture containing 14.8 % CO<sub>2</sub> and 85.2% N<sub>2</sub>, with activated carbon (0.5 g) as shown in Figure 12, but it was necessary to lower the flow rate (5 cc/min) to increase the contact time to utilize the full equilibrium adsorption capacity for CO<sub>2</sub> adsorption. This indicates that the rate of adsorption of CO<sub>2</sub>, on activated carbon at 1 atm was lower than that for the molecular sieve 13X.

## Conclusions

Molecular sieve 13X, 4A and activated carbon showed preferential adsorption of CO<sub>2</sub> at 25 °C and pressures up to 300 psi. Adsorption of CO<sub>2</sub> was found to be reversible on both molecular

sieve 13X and activated carbon. Equilibrium adsorption data from volumetric adsorption experiments indicated that the amount of CO<sub>2</sub> adsorbed on the molecular sieves is more than that of activated carbon at pressures less than 50 psi, but activated carbon showed significantly higher adsorption than molecular sieves at pressures above 50 psi. The equilibrium adsorption capacities of activated carbon, molecular sieve 13X and molecular sieve 4A at 300 psi and at 25 °C are about 8.5, 5.2, 4.8 moles of CO<sub>2</sub> /kg of the sorbent respectively. At 300 psi both molecular sieve 13X and activated carbon utilized the full capacity of the surface to form a close packed monolayer at the surface. Isosteric heats of adsorption calculations indicated that the molecular sieve 13X has a wide distribution of active sites for CO<sub>2</sub> adsorption. Potassium is preferentially distributed at the surface of the molecular sieve 13X and activated carbon. Excellent separation of CO<sub>2</sub> was obtained from gas mixtures containing both CO<sub>2</sub> /N<sub>2</sub> and CO<sub>2</sub> /H<sub>2</sub>/He utilizing both molecular sieve 13X and activated carbon during competitive gas adsorption studies performed with the micro reactor. However, it was necessary to use higher contact times of the gases with activated carbon than that with molecular sieve 13X to achieve the excellent separation.

## References

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Table I  
Elemental Ratios at the Bulk and the Surface

|       | <b>Bulk<br/>13X</b> | <b>Surf.<br/>13X</b> | <b>Bulk<br/>4A</b> | <b>Surf.<br/>4A</b> |      | <b>Bulk<br/>Act. C</b> | <b>Surf<br/>Act.C</b> |
|-------|---------------------|----------------------|--------------------|---------------------|------|------------------------|-----------------------|
| Al/Si | 0.75                | 1.08                 | 0.77               | 0.74                | Al/C | 0.0001                 | 0.023                 |
| Na/Si | 0.60                | 0.69                 | 0.54               | 0.78                | Na/C | 0.001                  | 0.005                 |
| K/Si  | 0.004               | 0.03                 | 0.04               | 0.04                | K/C  | 0.007                  | 0.041                 |